

Electroflotation for groundwater decontamination

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Abstract

An electroflotation device was built using a platinum-clad columbium screen as anode, and a stainless steel screen as cathode. A rock salt solution was used as the electrolyte, generating hypochlorite to oxidize cyanide, and hydroxides to form metal hydroxide precipitates which were carried to the top of the electroflotation device by the rising gas bubbles. The device was used successfully to remove Ni, Zn, Pb, Cu/CN in a polluted groundwater obtained from directly under a contaminated site, meeting the pretreatment standards of the pollutants for the local POWT sewer system. The cost of an electroflotation device plus a sand filter compares favorably with a conventional treatment system using cyanide oxidation/alkaline precipitation/ polymer-aided clarification. © 1997 Elsevier Science B.V.

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1. Introduction

Decontamination of sites and the groundwater at the sites is required by the Resources Conservation and Recovery Act (RCRA) as well as the Comprehensive Environmental Response, Compensation, and Liability Act. The technologies selected for groundwater decontamination vary depending on the type and quantity of pollutants in the groundwater. Another important factor for decontamination technology selection is the degree of treatment imposed by the regulating agency which is site specific. Often a train of treatment processes would be required to accomplish the treatment objectives. In general, a system to remove the bulk of the contaminants followed by a system to polish the quality of the treated groundwater is the minimum requirement.

This paper describes the quality of a groundwater obtained from directly under a contaminated site and the development of an electroflotation system for the groundwater treatment. The site is a medium size landfill that has in the past received industrial wastes in the northeast region. Metal plating wastes including different heavy metal species, cyanide, and solvents are known to be buried in various parts of the landfill.

Sampling of the groundwater directly under the site and analysis showed nickel, copper, lead, zinc and cyanide as the major contaminants in the groundwater from different locations, with Ni ranging from 75 to 125 mg/l, Cu 28 to 47 mg/l, Pb 9.8 to 35 mg/l, Zn 13 to 29 mg/l, and CN 82 to 191 mg/l.

A widely practiced technology in removing heavy metals from industrial process wastewater is precipitation followed by clarification. Chemical precipitation of metals employing lime, caustic soda or employing sulfides are effective. Other methods of metal removal including ion exchange, reverse osmosis, evaporation and activated carbon adsorption can each do a specific job effectively but are high in capital and operating costs. In addition, these technologies require more skilful operation and maintenance. Another emerging technology is to use microorganisms for cyanide and heavy metal removal. To date, most engineers use chemical precipitation–clarification with or without ion exchange polishing for metal removal, and chlorination for cyanide removal.

An electroflotation treatment system was developed for the decontamination of the groundwater with simultaneous removal of cyanide and Ni/Cu/Pb/Zn. It is a compact treatment system combining metal hydroxide flotation, metal oxidation/precipitation, and alkaline chlorination of cyanide all together in one treatment reactor. The reactor can remove all heavy metals to less than 0.50 mg/l and cyanide less than 0.05 mg/l.

2. Electroflotation process

Alkaline chlorination or peroxide oxidation can be very effective in cyanide removal. In the eastern European countries, electrolysis has been used for cyanide removal. An ample amount of sodium chloride is added to the cyanide-bearing waste before the solution is passed through an electrolytic cell. Hypochlorite is generated within the cell as the mixed solution is electrolyzed and the reaction takes place in the receiving tanks which follow. Electrolysis of seawater can generate chlorine to oxidize cyanide and hydroxides to precipitate heavy metals. Taking advantage of the concurrent reaction, a compact reactor was developed (Poon and Soccia, 1980 and Poon, 1984) for simultaneous removal of cadmium and cyanide. In this flow-through reactor, the electrolysis of seawater generated hypochlorite which oxidized cyanide into harmless carbon dioxide and nitrogen gas, similar to the technology used by the electroplating industry to use chlorine gas or sodium hypochlorite in cyanide oxidation (Marin et al., 1979 and USEPA, 1985). The generated hydroxides raised the pH of the wastewater and formed cadmium precipitates which were carried to the top by rising gas bubbles. The system was in effect three reactors in one in which (a) cyanide oxidation, (b) cadmium alkaline precipitation, and (c) cadmium hydroxide floc flotation all took place simultaneously in one reactor. The compact system replaces the current technology of three tanks used in succession for cyanide oxidation, alkaline cadmium precipitation, and polymer-aided clarification respectively. The flotation process is particularly effective in removing small metal particulates which normally escape clarifiers. The floating scum contains the heavy metals from the wastewater and small quantities of calcium, magnesium and sodium from the seawater. The scum should be similar in chemical characteristics to the

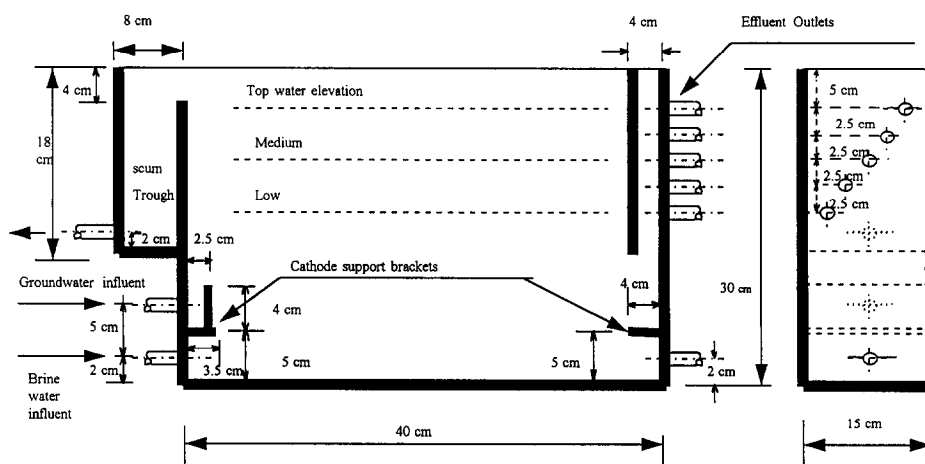


Fig. 1. Electroflotation reactor.

metal precipitates or sludge in the conventional method of alkaline precipitation. This form of metal concentrate can be shipped to facilities for disposal or for metal recovery.

In this study the seawater in the electroflotation reactor was replaced with rock salt solution at a concentration of 30 000 mg/l, which is equivalent to seawater NaCl concentration. The purpose was to demonstrate that the treatment system could be employed in areas without access to seawater. The electroflotation reactor was constructed with plexiglass with dimensions shown in Fig. 1. The rock salt solution or brine water entered and left the reactor at the bottom. The thickness of this brine water layer was kept at 5 cm. A stainless steel screen cathode was placed on top of the brine water layer supported by brackets. The anode, a platinum-clad columbium screen, was placed below the cathode with adjustable distance within the 5 cm space limitation.

The contaminated groundwater level in the reactor under treatment could be regulated by selecting one of the five effluent outlets. At the top level, the reactor contained a 20.6 cm layer of groundwater for treatment, or 10.67 liters (2.82 gal) above the cathode. At the medium and low levels, the respective volumes of groundwater above the cathode were 7.96 liters (2.1 gal) and 5.25 liters (1.39 gal). The dimensions for the noble metal anode were 32.4 cm by 12 cm, or 389 cm². By varying the groundwater and brine water pumping rates and controlling the groundwater level in the reactor, the hydraulic detention time for the brine water was kept within a range of 5.3 to 23.7 min and for the groundwater from 4.8 to 75 min.

The contaminated groundwater was stored in a 30 gal reservoir from which it was pumped by using a Masterflex pump with a variable speed drive to the electroflotation reactor through a control valve and flow meter. The groundwater entered the reactor into an inlet channel just above the cathode. The brine water was pumped from a 5 gal reservoir, through a control valve and a flow meter, into the reactor below the cathode. The spent brine water was drained back to the reservoir for recirculation without any wasting. The treated effluent passed through a sand filter before it was discharged to a

sewer. The sand filter was a 19 cm ID plexiglass column with a 30 cm layer of sand. The sand particles were 38% by weight larger than 3.5 mm nominal diameter, 86% by weight larger than 2.4 mm, and 95.5% by weight larger than 1.2 mm. The power supply unit for this work was EPSCO Filtered DC Power Supply, Model D-612T.

3. Work plan

There were three phases of work carried out in this study, including (1) batch study, (2) continuous flow study, and (3) copper recovery. The batch study identified the important process control variables. Continuous flow experiments were then designed statistically using the major control variables identified in the batch study. The effectiveness of the electroflotation process was measured. Finally a feasibility study of copper recovery by acidifying the metal scum followed by copper plating was attempted.

3.1. Batch study

Process variables readily identifiable for electroflotation include (1) groundwater pH, (2) metal and CN concentrations, (3) temperature, (4) groundwater depth in the reactor, (5) hydraulic detention time, (6) electrode spacing, and (7) power input. Only groundwater depth, hydraulic detention time, electrode spacing and power input are controllable. By combining the hydraulic detention time with volume of groundwater in the reactor, metal or cyanide removal, and power input, the mass of metal or cyanide removal per kilowatt-hour power consumption can be calculated. This dependent variable was used to gauge the treatment effectiveness of the electroflotation process throughout the entire study for both batch and continuous flow. By doing so, only three control variables were left for investigation in the batch study, namely groundwater depth (D), power input in watts (or current density), and electrode spacing.

After the space below the reactor was filled with the brine water and the contaminated groundwater was pumped to fill up to one of the five pre-determined outlet levels, power was switched on and regulated to a selected current density. For batch study, periodic adjustment of the power supply was required to maintain a constant current density. Periodic sampling and analysis of the metal and cyanide concentrations were carried out. It was observed that an electrode spacing of less than 2 cm would cause accumulation of gas bubbles in between the electrodes, which significantly reduced the electron flow and, consequently, caused a reduction of the treatment effectiveness. Electrode spacing of 3 cm or larger would bring better results and the treatment effectiveness, expressed in mg of metal or CN removed/kwh power consumption, did not vary noticeably from 3 to 4.5 cm electrode spacing. Consequently, a 3 cm electrode spacing was adopted for all batch and continuous flow throughout the study.

3.2. Continuous flow study

In the continuous flow study, each treatment was started as a batch process with a set of values of detention time, power input and groundwater depth. At the end of the

detention time, the brine water pump was turned on and the flow was regulated to give approximately 20 min retention time. The brine water leaving the reactor was drained back to its reservoir for complete recirculation. Next, the groundwater pump was turned on and regulated to provide a continuous flow and a predetermined hydraulic detention time. The treatment process was continued for a period of 3 to 4 times the hydraulic detention time or longer for periodic sampling. In order to facilitate a statistical analysis of the experimental results, the following design was used:

Experiment #	1	2	3	4	5	6	7	8	9
Groundwater	D_1	D_2	D_3	D_1	D_2	D_3	D_1	D_2	D_3
Depth									
Power Input	P_1	P_1	P_1	P_2	P_2	P_2	P_3	P_3	P_3
Treatment	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
Effectiveness (Dependent variable)									

The three depths used were 10.3, 15.45 and 20.6 cm. The three power inputs were P_1 from 0.011 to 0.012 A/cm², P_2 from 0.016 to 0.018 A/cm², and P_3 from 0.02 to 0.022 A/cm². The dependent variable E was mg metal or CN removed per kwh power consumption based on measurements.

3.3. Copper recovery

The floating scum from the copper/cyanide treatment study was collected and let stand in a clarifier for two hours. The settled heavy solids were collected and acidified with sulfuric acid until the pH was 1.64. Using a stainless steel anode and a copper plate cathode with 10.0 A at 5.5 V (approximately 0.24 A/cm²), the copper from the solution was plated out in 1.25 h. Copper concentrations before and after plating were determined. The material plated out onto the cathode had the appearance of a wet sludge of reddish yellow color typical of copper metal. The plated out material was removed from the cathode, dried in a vacuum desiccator, and weighed. The recovered material was analyzed for its copper content. The acidified solution contained mostly Cu, although small quantities of Mg, Ca and Na were present. The presence of Mg, Ca and Na in the acidified solution derived from the floating scum was caused by the rising gas bubbles which inadvertently carried some brine water into the groundwater under treatment in the electroflotation process. All metals plate out at different potentials in a plating process and the relative ease is reflected by the electromotive force series. With simple solutions at one molar ion concentration, $\text{Cu} = \text{Cu}^+$ is +0.52 V, $\text{Cu} = \text{Cu}^{2+}$ is 0.34 V while $\text{Mg} = \text{Mg}^{2+}$ is -2.37 V, $\text{Na} = \text{Na}^+$ is -2.715 V, and $\text{Ca} = \text{Ca}^{2+}$ is -2.87 V, according to Turner (1981). Complexing ions shift plating potentials to more negative values. Plating difficulty increases as the potential becomes more negative because of hydrogen co-deposition. The electropotential values above indicate that copper would be plated out much more easily and therefore can be recovered from the acidified solution.

3.4. Chemical analyses

Chemical analyses, including copper, nickel, lead, zinc, calcium, magnesium and sodium, followed the atomic absorption spectrometric procedure by direct aspiration into an air–acetylene flame (AA Perkin Elmer Model 3030B), residual chlorine measurement followed the orthotolidine procedure, total cyanide followed the distillation and titrimetric determination, chloride followed the mercuric nitrate method described in Standard Methods, 1985.

4. Results and data analysis

The purpose of the batch study was to identify the major process control variables affecting the metal and cyanide removal. The results indicated that the treatment effectiveness increased with groundwater depth and a detention time of 60 to 65 min would be adequate. Based on this information, two preliminary experiments were conducted in a continuous flow mode to confirm the results obtained from the batch study. Table 1 summarizes the results of these two preliminary studies which confirm the fact that a greater depth of groundwater in the reactor increased the treatment effectiveness. The hydraulic detention time required was approximately 75 min.

Groundwater samples from three different locations at the site were obtained for the continuous flow study. One contained mostly nickel. The second one contained mostly copper and cyanide. The third one contained mostly zinc and lead. The values of the control variables in the statistically designed experiments are listed in Table 2. The results of the continuous flow study for Ni removal are listed in Table 3, Cu–CN removal in Table 4, and Zn–Pb removal in Table 5. The data show very successful removal of all metals as well as cyanide in this compact electroflotation treatment process.

Nickel removal as shown in Table 3 was near completion in 60 min detention time. The effluent Ni concentration was 0.1 to 0.35 mg/l which would be able to meet the pretreatment standards of most POWT sewer systems. The chloride concentration varied between 4611 and 7260 mg/l in the treated effluent which meets the local POWT

Table 1
Preliminary experiments with continuous flow with copper–cyanide groundwater

Parameter		Expt. No. 1	Expt. No.2
Groundwater depth (<i>D</i>), [cm]		15.45	10.3
Power input (<i>P</i>), [W]		34.2	35.5
Influent	Cu conc., [mg/l]	37.78	39.93
	CN conc., [mg/l]	114	120
Effluent	Cu conc., [mg/l]	0.28	0.13
	CN conc., [mg/l]	0.07	0.19
Hydr. detention time, [min]		75	75
Treatment	mg Cu removal per kW h consumption	7034	4748
Effectiveness (<i>E</i>)	mg CN removal per kW h consumption	21370	14293

Table 2
Values of control variables in continuous flow experiments

	D_1 , 10.30	D_2 , 15.45	D_3 , 20.60	D_1 , 10.30	D_2 , 15.45	D_3 , 20.60	D_1 , 10.30	D_2 , 15.45	D_3 , 20.60	D_1 , 10.30	D_2 , 15.45	D_3 , 20.60
Metal and hydr. detention time	Groundwater depth [cm]											
Ni hydr. detention time/60 min	P_1 , 20.93	P_1 , 17.60	P_1 , 16.40	P_2 , 36.0	P_2 , 35.0	P_2 , 31.93	P_3 , 51.2	P_3 , 50.7	P_3 , 45.4			
Cu–CN hydr. detention time/75 min	P_1 , 22.05	P_1 , 20.01	P_1 , 22.60	P_2 , 36.1	P_2 , 35.80	P_2 , 37.50	P_3 , 54.50	P_3 , 62.50	P_3 , 60.30			
Zn–Pb hydr. detention time/75 min	P_1 , 17.55	P_1 , 18.00	P_1 , 20.40	P_2 , 35.70	P_2 , 38.35	P_2 , 37.50	P_3 , 51.00	P_3 , 54.00	P_3 , 56.40			

Table 3
Continuous flow experiments for Ni removal (60 min hydraulic detention for all experiments)

Parameter	Experiments								
	1	2	3	4	5	6	7	8	9
Groundwater depth (D), [cm]	10.30	15.45	20.60	10.30	15.45	20.60	10.30	15.45	20.60
Power input (P), [W]	20.93	17.60	16.40	36.00	35.00	31.93	51.20	50.70	45.40
Current density, [A/cm^2]	0.012	0.011	0.011	0.019	0.018	0.016	0.022	0.022	0.020
Treatment effectiveness (E), [mg Ni/kWh]	20.097	37.900	80.142	11.860	20.118	30.182	10.696	16.276	28.437
Initial Ni conc., [mg/l]	80.40	83.80	125.23	81.66	88.83	90.60	104.50	103.80	121.10
Effluent Ni conc., [mg/l]	0.28	0.19	0.35	0.33	0.27	0.28	0.19	0.13	0.10
Effluent residual Cl_2 conc., [mg/l]	27–49	11–28	3–38	187–200	147–206	84–92	277–307	264–272	40–48
Effluent chloride (Cl^-) conc., [mg/l]	7260	5,910	6522	6735	6560	4611	6473	6622	6,223

pretreatment standards. The treatment effectiveness ranged from 10.7 to 80.1 g Ni removal per kilowatt-hour power consumption. The data confirmed the fact that the treatment effectiveness increased with groundwater depth and lower current density applied to the reactor. A multiple linear regression analysis of the data in Table 3 (rows 1, 2, and 4) yields the following equation:

$$E = 17149 - 905(P) + 2693(D), \text{ with } r^2 = 0.737 (r = 0.86),$$

where E = treatment effectiveness, mg of Ni removed /kwh consumption, P = power input in watts, and D = groundwater depth in centimeters. The performance equation indicates that groundwater depth had a more significant effect than power input (or current density) on the treatment effectiveness, as the regression coefficient for D is three times as large as that for P .

The treated effluent contained residual chlorine. Some chlorine gas penetrated the floating scum layer. It is important that the treatment system is installed in a well-ventilated area. The residual chlorine concentration in the effluent increased with power input. It is important to note that under the best treatment condition, i.e., greatest groundwater depth and lowest power input (experiment #3, Table 3), the best treatment effectiveness was achieved along with an effluent of the lowest residual chlorine concentration. The pH of the treated effluents for the entire study was between 7.86 and 10.58. It was also observed in the nickel removal study that a very small but noticeable amount of nickel oxide was formed which precipitated to the bottom of the electroflotation unit.

For successful removal of copper and cyanide simultaneously from the groundwater, it was found that a 75 min detention time was required, as shown in Table 4. The effluent contained 0.02 to 0.08 mg/l Cu and 0.02 to 0.16 mg/l total CN. The electroflotation process therefore replaced two treatment processes in normal practice, i.e., chemical precipitation of metal and chlorination for CN removal. A multiple linear regression analysis of the data yields the following equations:

$$\text{Copper, } E = 7669 - 226P + 593D, \text{ with } r^2 = 0.896 (r = 0.947),$$

$$\text{Cyanide, } E = 30108 - 829P + 2138D, \text{ with } r^2 = 0.726 (r = 0.852).$$

Similar to the nickel removal study, the groundwater depth had a more significant effect than the power input (or current density) on the treatment effectiveness. The chlorine generated from the brine water electrolysis destroyed the total cyanide with the excess amount partly escaping to the atmosphere and partly staying in the solution as residual chlorine. A shorter detention allowed for the treatment process would result in lower residual chlorine but higher copper concentration in the effluent. This is a trade-off that can be considered in each specific application of site decontamination.

For the groundwater containing both zinc and lead, a 75 min detention time yielded an effluent with 0.04 to 0.52 mg/l of Zn and 0.10 to 0.34 mg/l of Pb. The performance equations based on multiple linear regression analysis of the data in Table 5 are presented in the following:

$$\text{Zinc, } E = 2422 - 55P + 243D, \text{ with } r^2 = 0.91 (r = 0.95),$$

$$\text{Lead, } E = 10375 - 300P + 368D, \text{ with } r^2 = 0.819 (r = 0.90).$$

The results were consistent with that of Ni removal or Cu and CN removal in that the treatment effectiveness increased with increasing groundwater depth and lower power input or current density. The residual chlorine concentration in the effluents was consistently higher in this study. The scum was thicker and more viscous in nature, trapping more chlorine and thus raising the residual chlorine content in the effluent.

An attempt was made to recover copper from the floating scum collected from the study. A volume of scum, 1168 ml, was collected and was let stand in a container. After 2 h, the clear solution on the top was decanted. To the remaining solution, 140 ml of concentrated H_2SO_4 were added for pH adjustment. Tap water was then added to bring the total volume of the solution to 4300 ml. The plating was carried out in a procedure described previously in the Work Plan. For 1.25 h, a total of 2.07 g of copper were plated out from 2.72 g of copper in the plating solution, or a 76.1% recovery. In addition to copper, the recovered material also contained 0.005 g of Ca, 0.03 g of Mg, and 0.046 g of Na, giving approximately a copper purity of 96.2%. The copper recovery using the method described in this study was only marginally successful. No attempt was made to optimize the recovery process, which could be improved with a better designed plating reactor.

5. Prototype system design and cost analysis

The prototype system of an electroflotation treatment unit is designed for a flow rate of 5.0 gal/min (18.93 l/min). The unit has an effective treatment volume of 1418 liters with the anode positioned under the cathode and occupying an area of 13500 cm^2 . Groundwater depth above the cathode is 97.5 cm. Fig. 2 depicts the prototype elec-

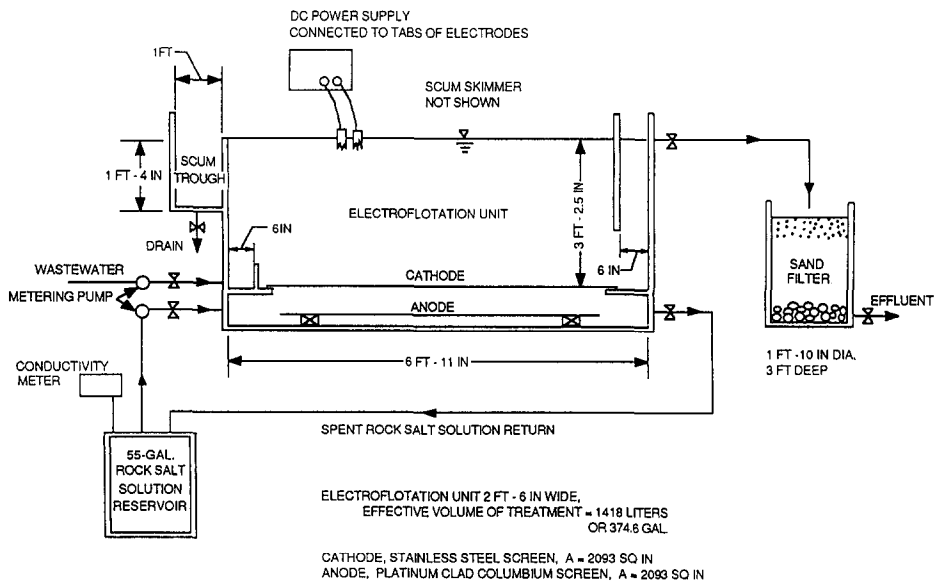


Fig. 2. Prototype electroflotation treatment system.

troflotation treatment unit showing the schematic diagram and the dimensions of the major components.

Cost estimation is provided in the following for the treatment system, using the 1995 dollar value. The polypropylene tank as the electroflotation unit as well as both the anode and cathode are custom-built with manufacture costs quoted by local firms in the northeast. Other cost information is obtained from equipment and chemical supply houses or catalog listings. Installation cost is estimated to be 25% of the capital cost for this system. Installed cost for a conventional treatment system is obtained from USEPA documents (USEPA, 1978a and USEPA, 1978b) and updated to 1995 dollar values for comparison. Sludge treatment and disposal cost is not included but is assumed to be identical for both systems.

Cost of electroflotation system

Electroflotation unit with automatic scum skimmer	\$16,686
Sand filter 22" dia., 3 ft deep, polyethylene tank, 2½ ft sand	250
Conductivity meter	790
	17,726
Installation cost, 25% × 17,726	4,432
Total system installed cost	
excluding contingency and engineering	\$22,158
Cost of conventional treatment system	
Cyanide oxidation unit, continuous flow	
5 gal/min, installed	\$16,445
Alkaline precipitation unit, continuous	
flow, 5 gal/min, installed	11,000
Flocculation/clarification unit, continuous	
flow, 5 gal/min, installed	11,500
Total system installed cost	
excluding contingency and engineering	\$38,945

There appears to be a saving of $\$38,945 - \$22,158 = \$16,787$, or approximately 43%, by using an electroflotation system. If cyanide does not exist in the groundwater, the cyanide oxidation unit for the conventional treatment system is not needed. In this case the cost of the electroflotation treatment system is about the same as that of the conventional treatment system.

6. Conclusions

This study shows that an electroflotation device can remove nickel, lead, zinc, copper/cyanide from a polluted groundwater at a contaminated site. The treated groundwater is able to meet the pretreatment standards of these pollutants for the local POWT sewer system at a cost compared favorably to a conventional treatment system using cyanide oxidation/alkaline precipitation/polymer-aided clarification. The elec-

troflotation device designed for groundwater decontamination needs further study in process optimization. Although metal recovery using the electroflotation device is feasible, the likely presence of a mixture of metals in contaminated groundwaters makes metal recovery impractical.

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